

**WORK PRODUCTION BY THERMODYNAMICALLY-REVERSIBLE,
IDEAL-GAS REACTIONS IN A VAN'T HOFF
CHEMICAL-POTENTIAL ENGINE**

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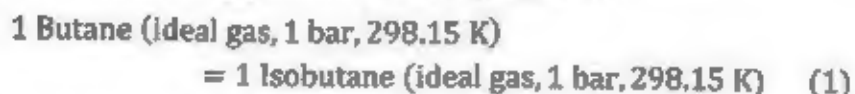
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Abstract

Once a number of fundamental thermodynamic notions associated to a reversible, ideal-gas phase chemical reaction were determined, among them the equation for its path, the equation for its driving force, and via this last one, the equation quantifying its work output at any given point along its unfolding, we proceeded to study in detail the occurrence of this reaction in a van't Hoff equilibrium box. The results obtained not only evinced the similarity existing between the way work is produced in both, the van't Hoff equilibrium box and Carnot's heat engine, but also the fact that like the latter, the former is also a cyclical process. The fundamental difference between the two being that while in Carnot's engine work is produced out of the heat transferred from a hotter to a colder heat reservoir, in van't Hoff's work comes out of the transfer of chemical matter between two different chemical states described by chemical potentials.

1. Introduction: The system of interest and its associated thermodynamic data.

The arguments to be here presented will be centered on the following thermodynamically-reversible, stoichiometric, isothermal, and isobaric chemical reaction taking place in the ideal-gas phase:



For the purposes of this discussion reversible is any process which in concatenation with its inverse restores the condition existing before any change had taken place, the so-called initial condition.

In the thermodynamic analysis of reaction (1) performed in the first six sections of this paper, the reaction system, namely pure butane at the initial state, pure isobutane at complete conversion, and any intermediate reaction mixture constitutes the system. The surroundings are constituted by a heat bath, in charge of maintaining the system's isothermal condition, and a mechanical or work reservoir acting as depository or supplier of the work either produced or demanded by the reaction system. These three bodies constitute the universe of the process. Serves to note that on reason of it taking place without change in total mole number, isothermal and isobaric reaction (1) is also isochoric, that is, it also evolves at constant volume. The relevant thermodynamic properties for this reaction are given in Tables 1, and 2.

Substance	ΔH_f°	ΔS_f°	ΔG_f°
butane	-126.1476	-0.3657	-17.1141
isobutane	-134.516	-0.3812	-20.8612

Table 1 Relevant standard thermodynamic data for butane and isobutane at 298.15 K (Stull et al., 1969, pp. 209, 245). ΔS_f° stands for the standard molar entropy of formation in $\text{kJ K}^{-1} \text{mol}^{-1}$, with ΔH_f° and ΔG_f° respectively representing the standard molar enthalpies, and standard molar Gibbs energies of formation, both in kJ mol^{-1} .

Reaction	ΔH° kJ mol ⁻¹	ΔS° kJ K ⁻¹ mol ⁻¹	ΔG° kJ mol ⁻¹
butane → isobutane	-8.3684	-0.0155	-3.7471

Table 2. Standard enthalpy, entropy, and Gibbs energy changes for reaction (1) per mole of reaction. These values were obtained as the difference of the corresponding enthalpies, entropies, and Gibbs energies of formation of isobutane minus those of butane given in Table 1.

2. The chemical potentials and the chemical force

The Gibbs energy change for a homogeneous, closed system capable of undergoing changes in composition, can be written as follows:

$$dG = VdP - SdT - dW \quad (2)$$

The previous equation can be obtained from the combination of the defining equations for the internal energy $dU = TdS - PdV - dW$; enthalpy $dH = dU + PdV + VdP$; and Gibbs energy $dG = dH - TdS - SdT$.

In eq. (2) dW represents work different from the work of displacement PdV , that is, different from:

... the work done by the system in displacing its environment at the steady pressure P ... (dW) is the chemical work ... a form of work which can be done by a system in the absence of any change of volume and due to its change of composition ...and which can be attained by use of the van't Hoff equilibrium box or the galvanic cell." (Denbigh, pp. 68, 81)

If the evolution of the system is isobaric and isothermal, then eq. (2) takes the following form:

$$-dG = dW \quad (3)$$

It is on reason of the state function nature of the Gibbs energy that the previous equation applies to both, the reversible as well as the irreversible transit of the system between identical initial and final states:

$$-dG = dW_{rev} = dW_{lost} \quad (4)$$

Or, equivalently

$$-\Delta G = W_{rev} = W_{lost} \quad (5)$$

Equations (4) and (5) make clear the fact that for isothermal and isobaric processes the Gibbs energy change represents the work transferred to the mechanical reservoir along the reversible path (W_{rev}), as well as the dissipated work-producing potential (W_{lost}) transferred in the form of heat to the heat reservoir along the irreversible path:

The change in G is, of course, the same for the same initial and final states of the reaction system, whether the process is conducted reversibly or not. It is the output of work which varies ... (Denbigh, p. 76)

A system undergoing change can perform maximum work only when the change is carried out reversibly. If the process is not completely reversible, the amount of work obtainable is always below the maximum, the difference appearing as heat. (Maron & Prutton, p. 189)

If the system under consideration turns out to be a homogeneous mixture of two components, α and β , then the following equation, making explicit the dependence of its Gibbs energy from temperature, pressure, and composition, also applies:

$$G = G(T, P, n_\alpha, n_\beta) \quad (6)$$

In what follows α is to be an alternative descriptor of butane, and β of isobutane, as they appear in reaction (1).

The total differential of eq. (6) has been written below:

$$dG = (\partial G / \partial T)_{P, n_i} dT + (\partial G / \partial P)_{T, n_i} dP + \sum_i (\partial G / \partial n_i)_{T, P, n_j} dn_i \quad (7)$$

The usual provisos apply regarding the n_i and n_j constraints appearing in the partial derivatives of the previous equation.

For a constant temperature and pressure evolution of the reaction system, the previous equation reduces to:

$$dG = \sum_i (\partial G / \partial n_i)_{T, P, n_j} dn_i \quad (8)$$

The comparison of equations (8) and (3) allows us to write:

$$dG = -dW = \sum_i (\partial G / \partial n_i)_{T, P, n_j} dn_i \quad (9)$$

The partial derivatives appearing on the right-hand side of equations (8) and (9), of capital importance in the thermodynamic theory of spontaneity, chemical, and phase equilibrium, are also represented in the following simpler manner:

$$\mu_i = (\partial G / \partial n_i)_{P, T, n_j} \quad (10)$$

This intensive quantity μ_i , with units of energy/mole, is the chemical potential of species i in the reaction mixture. As such, its value is dependent on the pressure, temperature, and composition of the said mixture.

The chemical potential of component i can be interpreted as the amount by which the capacity of the reaction mixture for doing work (other than work of expansion) increases per mole of i added at constant temperature, pressure, and composition. The following example provided by Denbigh might serve to make its meaning clearer:

...the chemical potential of copper sulphate in its aqueous solution in a Daniel cell is equal to the increased capacity of the cell to provide electrical energy, per mole of copper sulphate added (the addition actually being an infinitesimal). (Denbigh, p. 79)

Even if the 'infinitesimal addition' referred above by Denbigh is a way of satisfying the constant composition constraint implicit in eq. (10), a more sensible way to this end would have consisted in adding a small fraction of a mole of copper sulphate to a finite quantity of solution followed by the calculation of the proportionate increase per mol. "If (this) is done, for strict accuracy one must pass to the limit of $(\Delta G_i / \Delta n_i)$, as Δn_i approaches zero for the substance in question. The limit of this ratio, however, is exactly μ_i : $\mu_i = \lim_{\Delta n_i \rightarrow 0} (\Delta G_i / \Delta n_i)$ " (Aston & Fritz, p. 89; The quote includes minor changes in notation.)

In terms of the chemical potential, the following equivalent expressions for equations (8) and (9) will be written:

$$dG = \sum_i \mu_i dn_i \quad (11)$$

$$dW = - \sum_i \mu_i dn_i \quad (12)$$

Let us now bring here the thermodynamic variable known as the degree of advancement, or reaction coordinate ξ , defined as follows (Moore, pp. 283-284):

$$\xi = \frac{\Delta n_i}{\nu_i} \text{ mol} \quad (13)$$

In the previous equation Δn_i represents the change in number of moles experienced by chemical species i at the point at which ξ is being evaluated, with ν_i representing its unitless stoichiometric coefficient, negative for reactants, and positive for products. For reaction (1) it adopts the following forms:

$$\xi = \frac{\Delta n_i}{\nu_i} = \frac{n_\alpha - 1}{-1} = \frac{n_\beta - 0}{1} \quad (14)$$

From the previous expressions we get:

$$n_\alpha = 1 - \xi, \quad n_\beta = \xi \quad (15)$$

The fact that the total number of moles is equal to one:

$$n_\alpha + n_\beta = 1 - \xi + \xi = 1 \quad (16)$$

allows us to realize that the mole fractions (y_i) of these chemical species in the reaction mixture, as well as their respective partial pressures (p_i) in it, this on reason of the total pressure being equal to 1 bar, are numerically identical to their respective number of moles, as given by eq. (15), i.e.,

$$n_\alpha = y_\alpha = p_\alpha = 1 - \xi, \quad n_\beta = y_\beta = p_\beta = \xi \quad (17)$$

The corresponding differential expression for eq. (13) is given below:

$$dn_i = \nu_i d\xi \quad (18)$$

The substitution of eq. (18) in eq. (12) leads to:

$$dW = \left(- \sum_i \nu_i \mu_i \right) d\xi \quad (19)$$

In terms of the definition of work, thermodynamic or otherwise, as the product of force times displacement (Klotz & Rosenberg, p. 45), we can express dW as follows:

$$dW = \text{chemical force} \times \text{reaction's displacement} = f d\xi \quad (20)$$

A simple comparison between equations (19) and (20) allows us to identify the chemical force as the expression between parenthesis in eq. (19), i.e.,

$$f = - \sum_i \nu_i \mu_i \quad (21)$$

When the properly signed stoichiometric coefficients $v_\alpha = -1$ and $v_\beta = 1$ for reaction (1) are substituted in eq. (21), we get:

$$dW = (1\mu_\alpha - 1\mu_\beta) d\xi \quad (22)$$

The previous equation permits writing the following expression for the chemical force driving reaction 1 Butane \rightarrow 1 Isobutane:

$$f = 1\mu_\alpha - 1\mu_\beta \quad (23)$$

The following equation, coming out of the combination of equations (20) and (22), can now be written for reaction (1):

$$dW = (1\mu_\alpha - 1\mu_\beta) d\xi = f d\xi \quad (24)$$

The fact that $d\xi$ is, by definition, a measure of the change in the number of moles of reactants and products allows us to bring here the interpretation provided by Brønsted of the dW term appearing in the previous equations, as "... the work associated to the transport of chemical matter between two different chemical states described by chemical potentials." (Gill, p. 507)

The following statement of Maron & Prutton (p. 189, italics are ours), asserting that:

Work results only when the tendency of systems to attain equilibrium is harnessed in some way. *From a system in equilibrium no work can be obtained*, but a system in its way to equilibrium may be made to yield useful work.

will be given here the following representation:

$$\left(\frac{dW}{d\xi}\right)_{eq} = 0 \quad (25)$$

Combination of equation (25) with eq. (24) leads us to:

$$\left(\frac{dW}{d\xi}\right)_{eq} = 1\mu_{\alpha,eq} - 1\mu_{\beta,eq} = f_{eq} = 0 \quad (26)$$

The previous result allows us to trace this $(dW/d\xi)_{eq} = 0$ characteristic of a reaction in equilibrium to an even more fundamental condition: the fact that at this point the chemical force f —and with it the difference in chemical potentials it represents— is equal to zero, i.e.,

$$f_{eq} = 1\mu_{\alpha,eq} - 1\mu_{\beta,eq} = 0 \quad (27)$$

Once the chemical force has been re-expressed as a function of ξ , then the work associated, say, to the transit ($0 \rightarrow \xi$) of the reaction system, can be evaluated via the following integral:

$$Work = \int_0^{\xi} f(\xi) d\xi \quad (28)$$

3. Thermodynamic work

Work, says J. C. Maxwell (p. 54), "...is the act of producing a change of configuration in a system in opposition to a force which resists that change."

Regarding the work of expansion of a gas, the fact that "... for a given expansion the work performed depends upon the external pressure resisting the expansion..." makes it necessary to distinguish the (internal) pressure of the gas, P , from the external one, P_{ex} . "In order that an expansion may occur, the internal pressure, must, of course, be greater than the external, but this difference may be made as small as is desired, and as a limit we may consider the case in which the internal pressure is equal to the external pressure or differs from it by a negligible amount." The work produced under this condition is the reversible work. (Quotes from Pitzer and Brewer, p.35)

In general, while the work of expansion can be represented as $W = \int P_{ex} dV$; the reversible work, on its part, takes the following form $W_{rev} = \int P(V) dV$.

The previous statements require the following clarification:

While thermodynamics cannot do away with the infinitesimal difference between driving and resisting forces in reversible processes —making them equal makes the process impossible; mathematics certainly can, this on reason of the fact that the numerical results obtained with one or the other are for all practical purposes, identical.

This seems the proper place state that reversible processes are ideal, that is, practically impossible processes, and this is on reason of the impossibility of achieving an infinitesimal difference between driving and resisting forces. It is not uncommon to find the impossibility of reversible processes also defined in the following manner: "Strictly speaking, all reversible processes are impossible in nature, as they would require an infinite time for their accomplishment." (Maron & Prutton, p. 110) Even if practically unrealizable, the fact that they represent the efficient limit to natural processes, makes of them an indispensable tool for the theoretical analysis of thermodynamic processes.

Now, the following words from Denbigh (p.78):

The chemical potential has an important function analogous to temperature and pressure. A temperature difference determines the tendency of heat to pass from one body to another and a pressure difference determines the tendency towards bodily movement... a difference of chemical potential may be regarded as the cause of a chemical reaction or of the tendency of a substance to diffuse from one phase to another. The chemical potential is thus a kind of 'chemical pressure' and is an intensive property of a system, like the temperature and pressure themselves.

allows us to make a simile (with all the appropriate reservations) between the chemical force given above by eq. (21), and the internal pressure of the gas. The internal qualifier comes on reason of the fact that the chemical force finds definition in terms of the chemical potential of the substances constituting the reaction system; it is thus, as Denbigh notes, a property of the system, just like P is a property of the gas.

Just like the equation $W_{rev} = \int P(V)dV$ is used under the assumption that a pressure infinitesimally smaller than that of the gas is resisting the expansion, the same can be done with equation $W_{rev} = \int f(\xi)d\xi$ to evaluate the chemical work. This procedure de facto exempts us to provide any details as to the nature of this resisting force, or about the mode in which it performs its opposing or resisting role. Further comments on this issue in the discussion section. All we need to know to perform these integrations is knowledge of the functional relation connecting P and V in the former, and f with ξ in the latter. The interesting thing to be noted here is that even if f is the explanation for the occurrence of the reaction, and $f d\xi$ is the quantifier of its reversible work output, this pair plays, however, no role in the *actual* production of this work. As will be seen below, for chemical reactions taking place in the van' Hoff equilibrium box, this task, the actual production of work is carried on by the pair PdV . A similar thing happens in heat engines. While it is a temperature difference the one driving the flow of heat from the hot to the cold reservoir, work appears in the surroundings via the net result of two isothermal and reversible volume changes: one expansion, and one compression.

Even, if the work defined by the integral $W_{rev} = \int f(\xi)d\xi$ is, as made explicit by the 'rev' subscript, reversible work, it also quantifies, for an irreversible transit between the same initial and final states, the work lost in it. Being this so, we will abstain from attaching any superscript to W .

4. The functional connection between chemical force and reaction extent or degree of advancement in reaction (1)

According to Denbigh (p. 115):

... a gaseous mixture (is) said to be perfect if the chemical potential of each of its components is given by the following relation, in which μ_i^0 is a function of temperature only,

$$\mu_i = \mu_i^0 + RT \ln P + RT \ln y_i$$

Where P is the total gas pressure and y_i is the mole fraction of component i . Now, since μ_i^0 is independent of composition it retains the same value when y_i is brought up to unity. It is thus precisely the ... value of the Gibbs free energy per mole of the gas i in its pure state at unit pressure.

This equation ... can be put in a more compact form by means of the partial pressure p_i . Thus

$$\mu_i = \mu_i^0 + RT \ln p_i \quad (29)$$

The combination of the previous equation with the relations established by eq. (17), allows us to write the chemical potentials of butane and isobutane, and the chemical force by them defined, as they all pertain to reaction (1), in the following manner:

$$\mu_a = \mu_a^0 + RT \ln(1 - \xi) \quad (30)$$

$$\mu_b = \mu_b^0 + RT \ln(\xi) \quad (31)$$

$$f = 1[\mu_a^0 + RT \ln(1 - \xi)] - 1[\mu_b^0 + RT \ln(\xi)] \quad (32)$$

After rearrangement and simplification, the previous equation becomes:

$$f = -\Delta\mu^0 - RT \ln\left(\frac{\xi}{1 - \xi}\right) \quad (33)$$

Further replacement of $\Delta\mu^0$ for the standard Gibbs energy change of reaction (1), produces:

$$-f = \Delta G^0 + RT \ln\left(\frac{\xi}{1 - \xi}\right) \quad (34)$$

In which case, and in accord with equations (4), (24), and (34), we can write the following equation:

$$dG = -dW = -fd\xi = \left[\Delta G^0 + RT \ln\left(\frac{\xi}{1 - \xi}\right) \right] d\xi \quad (35)$$

Which can also be written as follows:

$$\frac{dG}{d\xi} = -\frac{dW}{d\xi} = \Delta G^{\circ} + RT \ln\left(\frac{\xi}{1-\xi}\right) \quad (36)$$

Applying the equilibrium condition stated above in eq (25), which given eq (4) can also be expressed as $\left(\frac{dG}{d\xi}\right)_{eq} = 0$, we obtain the well-known equation:

$$\Delta G^{\circ} = -RT \ln\left(\frac{\xi}{1-\xi}\right)_{eq} = -RT \ln K \quad (37)$$

While $\left(\frac{dW}{d\xi}\right)_{eq} = 0$ expresses, on one side, that at the state of equilibrium, as the previous quote of Maron and Prutton states, no more work can be obtained from a reversible chemical reaction, nor dissipated by an irreversible one; the $\left(\frac{dG}{d\xi}\right)_{eq} = 0$ condition identifies, on the other side, the state of equilibrium as the minimum of the graph G - vs. $-\xi$:

The criterion of equilibrium for a system of prescribed temperature and pressure is that G has reached its minimum possible value. (Denbigh, p. 83)

5. Numerical values for the chemical potentials and the chemical force for reaction (1)

With $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and the respective standard Gibbs energies of formation of butane, and isobutane at 298.15 K, namely $-17,114.1 \text{ J mol}^{-1}$ and $-20,861.2 \text{ J mol}^{-1}$, we will have equations (30), (31), and (32) taking the following forms:

$$\mu_{\alpha} = -17,114.1 + 2478.8 \ln(1-\xi) \text{ J mol}^{-1} \quad (38)$$

$$\mu_{\beta} = -20,861.2 + 2478.8 \ln(\xi) \text{ J mol}^{-1} \quad (39)$$

$$f = 1\mu_{\alpha} - 1\mu_{\beta} = 3747.1 + 2478.8 \ln\left(\frac{\xi}{1-\xi}\right) \text{ J mol}^{-1} \quad (40)$$

The evolution of these magnitudes along the course of reaction (1) can be read from Table 3, constructed by the simple expedient of substituting a few selected values of ξ into each of the three equations given immediately above, and performing the indicated operations.

In column 1 of Table 3, $\xi_{eq} = 0.82$ was calculated by solving eq (37) once $\Delta G^{\circ} = -3747.1 \text{ J mol}^{-1}$, and $RT = 2478.8 \text{ J mol}^{-1}$ were substituted in it.

The combination of equations (28) and (34) produces the following equation for the work associated to reaction (1):

$$W = \int -[\Delta G^{\circ} + RT \ln(\frac{\xi}{1-\xi})] d\xi \quad (41)$$

Performance of the previous indefinite integral produces.

$$W = -\xi \Delta G^{\circ} - RT[\xi \ln(\xi) + (1-\xi) \ln(1-\xi)] - RT + C$$

The constant of integration C in the previous equation, evaluated with the known fact that at complete conversion, $\xi = 1$, it is true that $W = -\Delta G^{\circ}$, turns out to be equal to $C = RT$, in which case, we can write it in the following manner:

$$W = -\xi \Delta G^{\circ} - RT[\xi \ln(\xi) + (1-\xi) \ln(1-\xi)] \quad (42)$$

The substitution in eq (42) of the thermodynamic magnitudes there involved produces, in turn, the following equation:

$$W = 3747.1 \xi - 2478.8 [\xi \ln(\xi) + (1-\xi) \ln(1-\xi)] \quad (43)$$

It was via the simple expedient of substituting in eq (43) selected values for ξ , that the numbers for W appearing in columns 5 and 6 of Table 3 were obtained.

6. About the results consigned in Table 3

The results produced by equations (38), (39), and (40), for the chemical potentials of butane, isobutane, and for their difference, that is for the chemical force, at various degrees of advancement of reaction (1), are those respectively contained by columns 2, 3, and 4. In accord with their respective dependence of the concentration of butane and isobutane, we see μ_{α} decreasing, and μ_{β} increasing as the reaction progresses, up to that point, the state of chemical equilibrium, at which no more difference exists between them. In accord with these considerations, we see the chemical force transiting from an arbitrarily large magnitude at $\xi = 0$, to a value of zero at equilibrium. The work calculated with the previous equation, identical at every ξ with the negative of the corresponding Gibbs energy change, quantifies, as explained above, the work gained, that is the work available in the work reservoir at any given ξ along the reversible path, as well as the work lost at same degree of advancement, along the irreversible path. The numbers in column 5 corresponding to post-equilibrium ξ 's, applying only to the reversible path, are smaller than those corresponding to $\xi_{eq} = 0.82$. The decrease obeys to the fact that work must be

removed from the work reservoir in order to be spent in forcing the system to go beyond its equilibrium condition, that is, into the region of conversions of isobutane larger than $\xi_{eq} = 0.82$. Concomitant to the decrease in the work available in the work reservoir, we find, on reason of this work being done in the system, an increase in its Gibbs energy. For example, the 63 J decrease in the content of the work reservoir, from 4241 J to 4178 J, spent in pushing the system along the transition ($\xi_{eq} = 0.82$) \rightarrow ($\xi = 0.9$), appear as an increase in the system's Gibbs energy, from -4241 J to -4178 J along the same transition.

ξ	$-1 \mu_e$	$-1 \mu_f$	$f = \frac{-\partial \Delta G}{\partial \xi} = \frac{\partial W}{\partial \xi}$	$W = -\Delta G$	$W_f - W_i$
0.00	17114.1	∞	∞	0	0
0.10	17375.3	26568.8	9193.5	1180	1180
0.20	17667.2	24850.7	7183.5	1990	810
0.30	17998.2	23845.6	5847.4	2638	648
0.40	18380.3	23132.5	4752.2	3167	529
0.50	18832.3	22579.4	3747.1	3592	425
0.60	19385.4	22127.4	2742.0	3916	324
0.70	20098.5	21745.3	1646.8	4137	221
0.80	21103.6	21414.3	310.7	4238	101
$\xi_{eq} = 0.82$	21364.7	21353.1	≈ 0	4241	3
0.90	22821.7	21122.4	-1699.3	4178	-63
1.00	∞	20861.2	∞	3747	-431

Table 3. Column 1 in mol, Columns 2 through 4 in Joules/mol, and columns 5 and 6, in joules. The graphs of these numbers are shown in Figures 2 and 3.

That the numbers in column 5 for $\xi > \xi_{eq}$ do not apply to the irreversible path obeys to the fact that at no point along this path, including the state of chemical equilibrium, we find any work available in the work reservoir

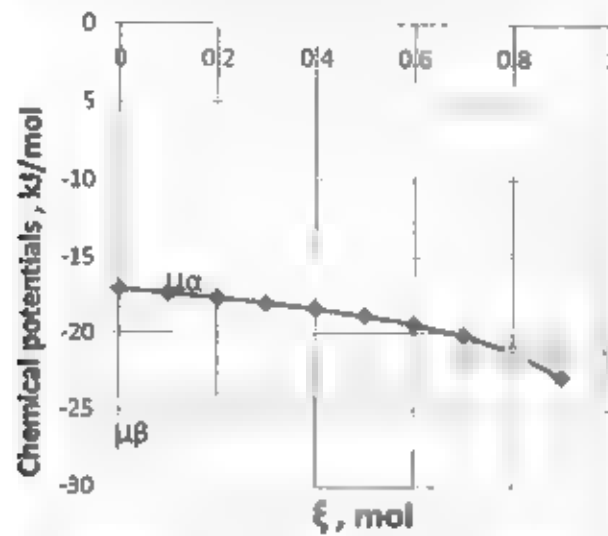


Figure 2 The chemical potentials of butane (α) and isobutane (β) vs. ξ .

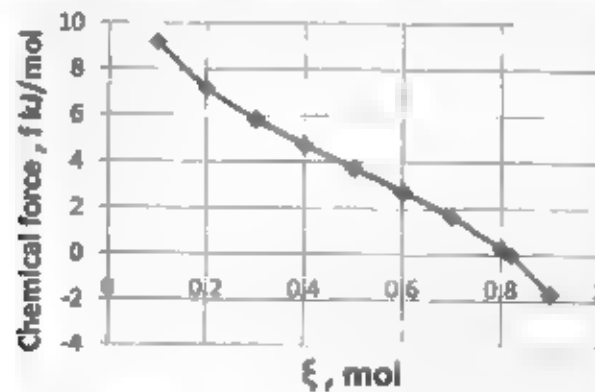


Figure 3 The chemical force f is positive for $\xi_{eq} < 0$, zero at $\xi_{eq} = 0.82$, and negative for $\xi_{eq} > 0$

It is this fact, the absence of available work in this irreversible universe, what makes any transit beyond the equilibrium condition, impossible. To make it happen we must re-define our universe to accommodate in it a new work-supplying body to carry on this task.

That the chemical force f is, as shown by equation (36), the instantaneous rate at which the work-producing potential of the reaction, as measured by ΔG , is being transformed into actual work along the reversible path, or dissipated into heat along the irreversible one, explains the heading of column 4.

The diminishing amounts of work produced (dissipated) as the reaction proceeds are the matter of the numbers in column 6. Thus, while the contribution of the transit from $(\xi = 0) \rightarrow (\xi = 0.1)$ amounts to 1180 J, the one from $(\xi = 0.1) \rightarrow (\xi = 0.2)$ reduces to 810 J, the one from $(\xi = 0.8) \rightarrow (\xi_{eq})$ only amounts to 3 J. This trend is a consequence of the fact that the value of the chemical force decreases as the reaction proceeds.

Let us now address the issue of how is it that the work producing potential of reaction (1) becomes gained work, that is, work available to us in a work reservoir

7. A thermodynamically-reversible chemical reaction in the ideal gas-phase

7.1 The isomerization of butane into isobutane in the van't Hoff Equilibrium Box

The present section is a modified version of the one appearing in a previous paper by this author on a related subject (Llúñez, 2014)

The detailed description of the mechanism through which the efficient conversion of the work producing potential of a chemical reaction into actual work takes place, will be done in what follows by studying the occurrence *at equilibrium* of reaction (1). The device in which this reaction is to take place, known as the van' Hoff equilibrium box (*EB*), has been represented in Figure 1

The operation of the *EB* for different types of chemical reactions, namely homogeneous reactions in the gas phase, and heterogeneous solid-gas reactions, has been described with various degrees of detail by Kauzmann, pp. 291-297, Denbigh, pp. 72-74, Smith and Van Ness, pp. 409-410; Fermi, pp. 101-106, and Pauli, pp. 54-56. among others.

The salient features of a reaction occurring at equilibrium in a van't Hoff equilibrium box, are the following:

1) It will take place without the production of work; conclusion which in terms of our previous discussions, finds explanation in the fact that at equilibrium it is true that $f_{eq} = 0$, and if so, also true that $dW_{eq} = f_{eq}d\xi = 0$. For such a reaction, the expression of the first law, $\Delta U = Q - W$, reduces to $\Delta U = Q$, which means that all the energy released by the reaction ends up as heat in its heat bath. The bath will later exchange some of this energy with a number of isothermal and reversible volume changes involving reactants and products, for it to be transformed, via the action of the pair PV , into the thermodynamically predicted maximum possible amount of work.

2) The final result of the operation to be described of the equilibrium box, takes the form of a standard reaction as in it the reactants remaining and the products produced appear in their pure states, that is separate from one another, each at the standard pressure of 1 bar at the temperature of the reaction.

The thermodynamic analysis starts with the reaction box, designated as C_R in Figure 1, containing a *vast* amount of reaction (1) in chemical equilibrium at 298.15 K and 1 bar total pressure. It is to this equilibrium mixture that n moles, $0 < n \leq 1$, out of the initial mole of butane available for reaction (1), will be added, and n moles of isobutane removed. It is in this vast amount of reaction mixture in equilibrium where we will see the said n moles of butane (α) introduced in it, isomerized into n moles of isobutane (β). The $(1 - n)$ moles of α remaining and the n moles of β produced will be found at the end, separate of one another, and each of them at 1 bar and temperature T .

The result of the four processes which described below, constitute van't Hoff's box mode of operation, can be represented as follows.



The brackets appearing in the right-hand side of the previous equation emphasize that these chemical species are found at the end of said four processes, separate from one another and at the indicated conditions.

Let us now center our attention on the situation depicted in Figure 1. In it C_α and C_β are cylinders fitted with weightless and frictionless pistons. The connection of the cylinders to the reaction box C_R includes valves V_α and V_β —initially closed— as well as semi-permeable membranes M_α and M_β ; the former permeable only to ideal gas α , the latter only to ideal gas β . The reaction box C_R

contains a vast amount of a mixture of gases α and β at their respective equilibrium pressures $P_{\alpha,eq}$, $P_{\beta,eq}$, at temperature T , i.e., in C_R .

$$\alpha(P_{\alpha,eq}, T) = \beta(P_{\beta,eq}, T) \quad (45)$$

The pressure inside the box is constant and equal to $P_{C_R} = P_{\alpha,eq} + P_{\beta,eq}$. The pistons have been properly coupled to a work or mechanical reservoir (*mr*) -not shown- whose function is to serve as deposit or provider of the work either produced or demanded by the operation. Initially, while cylinder α contains 1 mole of α at 1 bar and temperature T , cylinder β is empty, with its piston in its extreme leftmost position. At this point the pressures keeping these pistons in place are 1 bar, and $P_{\beta,eq}$, respectively. The equilibrium box is in thermal contact with a heat bath or heat reservoir (*bath*) -not shown- of temperature T .

Gases α and β in the cylinders, as well as their equilibrium mixture in the reaction box, constitute the thermodynamic system (*sys*); with the heat and mechanical reservoirs constituting the surroundings. Combined, system and surroundings constitute the universe of the process. The mechanical device constituted by reaction box, cylinders, pistons, valves, and semi-permeable membranes is called the *van't Hoff Equilibrium Box (EB)*.

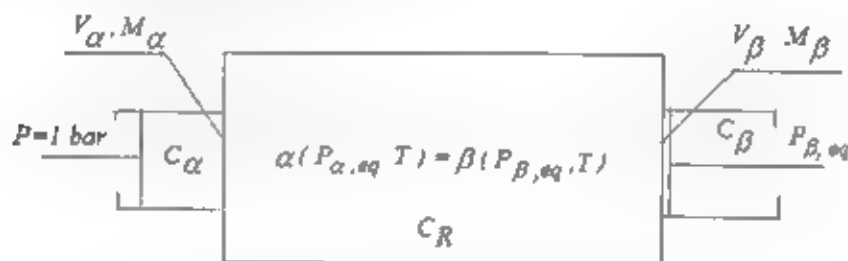


Figure 1. The van't Hoff Equilibrium Box.

The form of the first law to be here used to describe and quantify the energy exchanges of the system with its surroundings, is the following $\Delta U = Q - W$. In it, heat absorbed, and work done by the system are positive magnitudes, their inverses, negative. It is understood that in the universe just described, the only bodies capable of exchanging heat are the heat bath and the system, in which case heat lost by one, is heat gained by the other. Likewise, the only bodies capable of exchanging energy in the form of work are the system and the work or mechanical reservoir, in which case, work done by one is work done on the

other. It will be further assumed that the reader is knowledgeable about the thermodynamics of ideal gases.

7.2. The four processes taking place in the van't Hoff equilibrium box

Process 1: The mole of gas α in cylinder C_α is expanded isothermally (T) and reversibly from 1 bar to $P_{\alpha,eq}$. At the end of this process the pressure keeping this piston in place is $P_{\alpha,eq}$. In accordance with the isothermal nature of this process, and the sole dependence of the internal energy of ideal gases with the temperature, we will have:

$$\Delta U_{sys,1} = 0 \quad (46)$$

As indicated by the form adopted by the first law for this process, namely $Q_{sys} = W_{sys}$, the reversible work transferred by the system to the work reservoir, comes from an equivalent amount of heat absorbed by it from the heat bath. It is with base on these considerations that the following equation will be written.

$$-Q_{bath,1} = Q_{sys,1} = W_{sys,1} = -W_{mr,1} = -nRT \ln(P_{\alpha,eq}) \quad (47)$$

In it, the last term on the right-hand side quantifies, as should be known, the reversible work of expansion produced by the ideal gas in its transit from $P = 1$ to $P_{\alpha,eq}$. It should be noted that the argument of the logarithmic term in the previous expression is a quotient whose denominator, omitted here for reasons of economy of expression, is the unit valued initial pressure of the said expansion.

At the conclusion of this process both valves are opened for Process 2 to occur.

Process 2. Here n moles of gas $\alpha(P_{\alpha,eq}, T)$ are introduced into the reaction box, and n moles of gas $\beta(P_{\beta,eq}, T)$ simultaneously removed from it, $0 < n \leq 1$. The respective representations of these two processes, given below:

$$\begin{aligned} [n\mu_\alpha(p_{\alpha,eq}, T)]_{before\ addition} &= [n\mu_\alpha(p_{\alpha,eq}, T)]_{after\ addition} \\ [n\mu_\beta(p_{\beta,eq}, T)]_{before\ extraction} &= [n\mu_\beta(p_{\beta,eq}, T)]_{after\ extraction} \end{aligned}$$

allows us to realize that:

Since the fugacities are the same in the cylinder as in the mixture, there is no change in free energy; the process occurs at equilibrium (Smith and Van Ness, pp. 409-410)

The fact that no change in free energy means no exchange of energy in the form of work, leads us to:

$$W_{\alpha,2} = 0 \quad (48)$$

$$W_{\beta,2} = 0 \quad (49)$$

The combination of the work associated to these two processes determines the work of the system for Process 2:

$$W_{sys,2} = W_{\alpha,2} + W_{\beta,2} = 0 \quad (50)$$

The sub-indexes here used refer to the changes experienced by the system, in the form of gases α or β , in process 2

That the temperature of each of these two gases remained constant along the processes just described, means that they experienced no change in their internal energies, i.e.,

$$\Delta U_{sys,2} = \Delta U_{\alpha,2} + \Delta U_{\beta,2} = 0 \quad (51)$$

The substitution of the two previous results in the equation for the first law, $\Delta U_{sys} = Q_{sys} - W_{sys}$, leads to the conclusion that

$$Q_{sys,2} = 0$$

The previous results evince the fact that no heat exchange takes here place between the system and the heat bath, that is:

$$Q_{bath,2} = Q_{sys,2} = 0 \quad (52)$$

Additional comments on this process can be found in Section 15.

At the conclusion of this process the valves are closed.

Process 3. Following the introduction/removal process just described, the following reaction takes place:



The fundamental assumption behind the *modus operandi* of the van' Hoff equilibrium box in general, and of reaction (53) in particular, or of the inverse of this reaction, is that even if the disequilibrium created on the vast amount of reaction in the reaction box by the addition of n moles of α , and the removal of n moles of β produces no measurable effect on the respective partial pressures or concentrations of these two chemical species, it will be however (this disequilibrium) the reason for the occurrence of reaction (53) through which equilibrium in the box will be restored.

In Fermi's words:

We assume that the content of the large box is so great that the relative changes in concentration resulting from this inflow of gases is negligible. The concentrations of the gases during this process, therefore, remain practically constant. Moreover, since the temperature and volume of the large box do not change, the chemical equilibrium of the gases in the box readjusts itself... (pp. 103, 105).

The fact that in this reaction butane at its equilibrium conditions is transformed into isobutane at the same conditions is the reason why this reaction is said to be taking place 'at equilibrium.' The fact shown above in eq (27), that at equilibrium the chemical force is zero, means that the occurrence of reaction (53) will take place without any exchange of work with its work reservoir

$$\text{If } f_{eq} = 0, \text{ then } W_{sys,3} = 0 \quad (54)$$

At the light of the previous result, the expression of the first law for reaction (53), that is for the system in process 3, namely $\Delta U_{sys,3} = Q_{sys,3} - W_{sys,3}$, reduces to:

$$\Delta U_{sys,3} = Q_{sys,3} \quad (55)$$

The previous equation shows that the whole of the internal energy or enthalpy change of reaction (53), which is the energy coming from the breaking and forming of chemical bonds defining this chemical process, appears as an equivalent amount of heat.

The situation to be noted at this point in process 3 is that there exists no avenue open, no mechanism at play which could take this energy (the thermodynamically mandated fraction of it, that is), as it is being made available by reaction (53) and transform it into work. The only path open to it is the one leading to the heat bath, and it is this fact what defines the way through which the said fraction of this energy is to be converted into work.

Let us acknowledge now the following two facts. 1) The internal energy, and the enthalpy, of an ideal gas are sole functions of its temperature (Denbigh, p. 113). The previous statement implies that said functions are independent from the pressure; 2) Any ideal-gas phase, isothermal, and isobaric reaction taking place with constant total mole number, $\Delta n = 0$, like the one being here considered, is also isochoric, and on reason of this, for any such reaction the internal energy and enthalpy changes become identical: $\Delta U = \Delta H - P\Delta V = \Delta H - RT\Delta n = \Delta H$

It is with the previous notions in mind that the following equation will be written:

$$\Delta U_{sys,3} = \Delta H_{sys,3} = \Delta H[n\alpha(p_{\alpha,eq}, T) \rightarrow n\beta(p_{\beta,eq}, T)] = n\Delta H[\alpha(1\text{bar}, T) \rightarrow \beta(1\text{bar}, T)] = n\Delta H^\circ = n\Delta U^\circ \quad (56)$$

From which the following equation will be excerpted:

$$\Delta U_{sys,3} = n\Delta U^\circ = n\Delta H^\circ \quad (57)$$

The combination of equations (55) and (57) leads us to the following equation in which we have included the change experienced by the heat bath.

$$n\Delta H^\circ = Q_{sys,3} = -Q_{bath,3} \quad (58)$$

Process 4. Here, the amounts of α and β in C_α and C_β at the end of process 3, namely $(1-n)\alpha(p_{\alpha,eq}, T)$ and $n\beta(p_{\beta,eq}, T)$, will be now compressed isothermally (T) and reversibly to a final pressure of 1 bar. The amounts of work involved are the following.

$$W_{\alpha,4} = Q_{\alpha,4} = -Q_{bath,\alpha,4} = (1-n)RT \ln p_{\alpha,eq} \quad (59)$$

$$W_{\beta,4} = Q_{\beta,4} = -Q_{bath,\beta,4} = nRT \ln p_{\beta,eq} \quad (60)$$

Combined, the two previous equations quantify the changes experienced by the system and the bath in this process in the following manner:

$$\begin{aligned} W_{sys,4} = W_{\alpha,4} + W_{\beta,4} &= Q_{sys,4} = -Q_{bath,4} \\ &= (1-n)RT \ln p_{\alpha,eq} + nRT \ln p_{\beta,eq} \end{aligned} \quad (61)$$

The isothermal nature of these two processes means that they occur without changes in their respective internal energies. This fact is implicit in the equality between work and heat evinced by the previous three equations. Therefore.

$$\Delta U_{sys,4} = 0 \quad (62)$$

7.3 A summary of changes

7.3.1 The reaction Box

No change remains in the reaction box once the previous processes have concluded. The original changes consisting in the addition of n moles of α and the simultaneous removal of n moles of β were offset by the occurrence of reaction $n\alpha(p_{\alpha,eq}, T) \rightarrow n\beta(p_{\beta,eq}, T)$ through which the n moles of α inserted were consumed in order to replenish the n moles of β extracted; with the constancy of its temperature assured by the action of the heat reservoir

7.3.2 The Cylinders

Cylinders α and β do experience changes in their respective conditions because of these four processes. Thus, while the former originally contained 1 mole of

$\alpha(1\text{ bar}, T)$, at the end it contains only $(1 - n)$ moles of this gas at these same conditions. The latter, originally empty, is found at the end containing n moles of $\beta(1\text{ bar}, T)$. Note then that the previous concatenation of processes has managed to reversibly transform the original mole of $\alpha(1\text{ bar}, T)$ into pure α and pure β in the amounts and conditions given by $(1 - n)\alpha(1\text{ bar}, T)$, and $n\beta(1\text{ bar}, T)$. The former occupying cylinder α and the latter cylinder β . In other words, these four processes combined to bring forward the reversible standard reaction given by equation (44).

7.3.3 The System

The work performed by the system along these four processes, quantified in equations (47), (50), (54), and (61), amounts to:

$$W_{sys} = -RT \ln P_{\alpha,eq} + 0 + 0 + (1 - n)RT \ln P_{\alpha,eq} + nRT \ln P_{\beta,eq} \quad (63)$$

Upon simplification, this equation reduces to:

$$W_{sys} = nRT \ln \left(\frac{P_{\beta,eq}}{P_{\alpha,eq}} \right) \quad (64)$$

Recognition of the fact that the pressure quotient in the previous equation is the equilibrium constant K for reaction (1) at temperature T , combined with the fact that:

$$\Delta G^o = -RT \ln K \quad (65)$$

Allows writing equation (64) as follows:

$$W_{sys} = -n\Delta G^o \quad (66)$$

The heat exchanged by the system in each of these processes has been evaluated in equations (47), (52), (58), and (61). It amounts to:

$$Q_{sys} = -RT \ln P_{\alpha,eq} + 0 + n\Delta H^o + (1 - n)RT \ln P_{\alpha,eq} + nRT \ln P_{\beta,eq} \quad (67)$$

Simplification of this equation, followed by its combination with equation (65) produces:

$$Q_{sys} = n(\Delta H^o - \Delta G^o) \quad (68)$$

The defining equation of the Gibbs energy, $G = H - TS$, allows writing the previous expression as

$$Q_{sys} = nT\Delta S^o \quad (69)$$

The internal energy changes experienced by the system are given in equations (46), (51), (57), and (62). Combined, they amount to:

$$\Delta U_{sys} = 0 + 0 + n\Delta H^{\circ} + 0 = n\Delta H^{\circ} \quad (70)$$

The final form of the previous equation comes through the substitution in the equation for the first of the results shown in equations (66) and (67), i.e.,

$$\Delta U_{sys} = n\Delta H^{\circ} = Q_{sys} - W_{sys} = n(T\Delta S^{\circ} + n\Delta G^{\circ}) \quad (71)$$

7.3.4 The mechanical reservoir

That in the universe of the equilibrium box the only bodies capable of exchanging energy in the form of work are the system and the work reservoir (*mr*) means that work done by one is work done on the other, and vice-versa. In other words, $W_{sys} = -W_{mr}$. According to this, at the end of the four processes above described, the work in the work reservoir finds, in attention to eq. (66), the following quantification:

$$W_{sys} = -W_{mr} = -n\Delta G^{\circ} \quad (72)$$

It should be kept in mind that while ΔG° in the previous equation is a constant which stands for the difference between the standard Gibbs energies of formation of 1 mole of isobutane and 1 mole butane, as they appear in reaction (1), both work terms there appearing W_{sys} , and W_{mr} , refer to the conversion of n moles of butane into isobutane, $0 < n \leq 1$. As expressed in the previous equation, both these terms are functions of n .

7.3.5 The heat reservoir

That in the universe of the equilibrium box the only bodies capable of heat exchange are the system and the heat bath means that heat gained by one is heat lost by the other. According to this, and in attention to eq. (69), we can quantify the heat exchanged by the heat bath with the following expression:

$$Q_{bath} = -nT\Delta S^{\circ} \quad (73)$$

All the results obtained in the previous discussion agree with thermodynamic theory.

Regarding the standard isomerization reaction of butane into isobutane, we have this exothermic reaction making available in process 3, an amount of heat equal to $n\Delta H^{\circ} = n \cdot 8368.4 \text{ J}$ which is originally transferred to the heat bath. A portion of this energy in the amount of $n\Delta G^{\circ} = n \cdot 3747.1 \text{ J}$ leaves the heat bath to be transformed into an equivalent amount of work that ends up in the work reservoir. The difference, in the amount of $n \cdot T\Delta S^{\circ} = n(298.15 \cdot 15.5) = n \cdot 4621.3 \text{ J}$ remains, as unavailable energy, in the heat bath.

8. Back to the beginning

It was through the concatenation of the four processes just described that the following reaction, as represented in eq (44), took place.



This new concatenation of the four processes to be described below, will be responsible on the other hand, for the inverse change, namely.



The processes and associated changes subsumed by it, will be identified with Roman numerals. When necessary, these processes/changes will also bear the subscript $\beta \rightarrow \alpha$ to distinguish them from those associated to the previous concatenation, which, when needed, will be identified by the subscript $\alpha \rightarrow \beta$.

The new concatenation starts at the conditions we find the universe (system and surroundings) at the conclusion of the previous one. Here, the achievement of the intended change represented in eq. (74) will include, among other processes, the occurrence of the inverse of reaction (53), that is, of reaction:



The description of these four new processes is given below.

Process I: Gases α and β , in the amounts and conditions they are respectively found in cylinders C_α and C_β at the conclusion of the previous concatenation, namely $(1-n)\alpha(1 \text{ bar}, T)$, and $n\beta(1 \text{ bar}, T)$, will be isothermally and reversibly expanded to respective pressures $P_{\alpha,eq}$ and $P_{\beta,eq}$. The following changes accompany these expansions:

$$\Delta U_{sys,I} = 0 \quad (76)$$

$$\begin{aligned} W_{sys,\alpha,I} = Q_{sys,\alpha,I} = -Q_{bath,\alpha,I} = -W_{mr,\alpha,I} \\ = -(1-n)RT \ln(P_{\alpha,eq}) \end{aligned} \quad (77)$$

$$W_{sys,\beta,I} = Q_{sys,\beta,I} = -Q_{bath,\beta,I} = -W_{mr,\beta,I} = -nRT \ln(P_{\beta,eq}) \quad (78)$$

The fact that $W_{sys,I} = W_{sys,\alpha,I} + W_{sys,\beta,I}$, leads us to the following expression:

$$\begin{aligned} W_{sys,I} = Q_{sys,I} = -Q_{bath,I} = -W_{mr,I} \\ = -(1-n)RT \ln(P_{\alpha,eq}) - nRT \ln(P_{\beta,eq}) \end{aligned} \quad (79)$$

After rearrangement and simplification, the previous equation takes the following form

$$\begin{aligned}
W_{sys,I} = Q_{sys,I} = -Q_{bath,I} = -W_{mr,I} \\
= -RT \ln(P_{\alpha,eq}) + nRT \ln(P_{\alpha,eq}) - nRT \ln(P_{\beta,eq}) \\
= -RT \ln(P_{\alpha,eq}) + nRT \ln\left(\frac{P_{\alpha,eq}}{P_{\beta,eq}}\right) \\
= -RT \ln(P_{\alpha,eq}) - n\Delta G_{\beta \rightarrow \alpha}^0 \quad (80)
\end{aligned}$$

Process II. The fact that the addition/removal process taking place here is essentially the same as that discussed in process 2, allows us to identify the introduction of n moles of gas $\beta(P_{\beta,eq}, T)$ into the reaction box, and the removal from it of n moles of gas $\alpha(P_{\alpha,eq}, T)$ from it, as processes taking place with no change in Gibbs energy, and if so, without any exchange of energy in the form of work. Therefore:

$$W_{\alpha,II} = 0 \quad (81)$$

$$W_{\beta,II} = 0 \quad (82)$$

Note here that at the conclusion of this process we will find that while C_{α} contains 1 mole of α , C_{β} is, on its part, empty.

The combination of the two previous equations produces:

$$W_{sys,II} = 0 \quad (83)$$

From the isothermal nature of these two processes, we get:

$$\Delta U_{sys,II} = 0 \quad (84)$$

And from the first law, in the form $Q_{sys,II} = \Delta U_{sys,II} + W_{sys,II}$, the following result is produced:

$$Q_{sys,II} = 0 + 0 = 0 \quad (85)$$

Process III. It is in this process where, via eq. (75), the n extra moles of β in the reaction mixture are consumed to offset its n moles of α deficit. The fact that it is a reaction taking place 'at equilibrium,' means, as already noted regarding these reactions, that no work is exchanged by it, if so, then:

$$W_{sys,III} = 0 \quad (86)$$

In terms of the previous result, the first law reduces to:

$$\Delta U_{sys,III} = Q_{sys,III} \quad (87)$$

The fact made evident by a simple inspection of eq (56) that $\Delta U_{sys,III} = -\Delta U_{sys,3}$ allows us, on reason of eq. (57), to re-express eq. (87) in the following manner:

$$\Delta U_{sys,III} = Q_{sys,III} = \Delta H_{\beta \rightarrow \alpha}^{\circ} \quad (88)$$

The previous equation shows that along its occurrence, reaction (75) takes away from the heat bath an amount of heat equal to $\Delta H_{\beta \rightarrow \alpha}^{\circ}$, identical in magnitude to that transferred to the heat bath by reaction (53) in process 3.

The following quote from Clausius serves to set processes 3, and III, in the proper thermodynamic frame:

let us consider a cyclical process, which is such that a body passes through a series of changes of condition and at last returns to its original state. This variable body, if placed in connection with the heat reservoir to receive or give heat, must have the same temperature as the reservoir; for it is only in this case that the heat can pass as readily from the reservoir to the body as in the reverse direction, and if the process is reversible it is requisite that this should be the case. (p. 106)

Process IV. At this point the 1 mole of α in cylinder C_{α} is compressed isothermally and reversibly from $P_{\alpha,eq}$ to 1 bar. The changes associated to this process are the following:

$$\Delta U_{sys,IV} = 0 \quad (89)$$

$$W_{sys,IV} = Q_{sys,IV} = -Q_{bath,IV} = -W_{mr,IV} = RT \ln P_{\alpha,eq} \quad (90)$$

8.1 Summary of Changes for the inverse path.

8.1.1 Internal energy: From equations (76), (84), (88), and (89) we can write, for the internal energy change of the system along the inverse process (*inv*), the following equation:

$$\Delta U_{sys,inv} = 0 + 0 + n\Delta H_{\beta \rightarrow \alpha}^{\circ} + 0 = n\Delta H_{\beta \rightarrow \alpha}^{\circ} \quad (91)$$

8.1.2 Work: The work exchanged by the system is determined by the combination of equations (80), (83), (86), and (90):

$$W_{sys,inv} = -RT \ln(p_{\alpha,eq}) - n\Delta G_{\beta \rightarrow \alpha}^{\circ} + RT \ln(p_{\alpha,eq}) = -n\Delta G_{\beta \rightarrow \alpha}^{\circ} \quad (92)$$

8.1.3 Heat: The heat exchanged by the system with the heat bath can be obtained from equations (80), (85), (88), and (90):

$$\begin{aligned} Q_{sys,inv} &= -RT \ln(p_{\alpha,eq}) - n\Delta G_{\beta \rightarrow \alpha}^0 + 0 + n\Delta H_{\beta \rightarrow \alpha}^0 + RT \ln(p_{\alpha,eq}) \\ &= n(\Delta H_{\beta \rightarrow \alpha}^0 - \Delta G_{\beta \rightarrow \alpha}^0) = nT\Delta S_{\beta \rightarrow \alpha}^0 \quad (93) \end{aligned}$$

9. Summary of results for the cycle defined by the combination of the two previous concatenations

9.1 Internal energy: From the combination of equations (70) and (91) we get.

$$\Delta U_{sys,cycle} = \Delta H_{\alpha \rightarrow \beta}^0 + \Delta H_{\beta \rightarrow \alpha}^0 = 0 \quad (94)$$

The equality to zero of the previous equation stems from the state function nature of the enthalpy, which asserts that $\Delta H_{\alpha \rightarrow \beta}^0 = -\Delta H_{\beta \rightarrow \alpha}^0$.

9.2 Work: The work exchange by the system and the work reservoir, calculated with equations (72) and (92), leads us to the following result:

$$W_{sys,cycle} = -W_{mr,cycle} = -n\Delta G_{\beta \rightarrow \alpha}^0 - n\Delta G_{\alpha \rightarrow \beta}^0 = 0 \quad (95)$$

The zero in the previous equation finds the same explanation as that given for eq. (94).

9.3 Heat: The heat exchanged by the system with the heat bath, calculated with equations (69) and (93):

$$Q_{sys,cycle} = -Q_{bath,cycle} = nT\Delta S_{\alpha \rightarrow \beta}^0 + nT\Delta S_{\beta \rightarrow \alpha}^0 = 0 \quad (96)$$

Note that here, again, $nT\Delta S_{\alpha \rightarrow \beta}^0 = -nT\Delta S_{\beta \rightarrow \alpha}^0$.

Equations (94), (95), and (96), make evident the fact that at the completion of the cycle, no change remains in the system, the bath, or the work reservoir. At the end of this cycle, the universe has returned to its original condition, and no evidence remains of any change having ever taken place, which is the essential meaning of the reversibility concept, at least in the way it was originally understood by Carnot (pp. 11, 19). Said restoration implies the reversibility of both, the forward, and reverse processes.

The introduction into the reaction box, in the first concatenation, of only a fraction n of the one mole of available butane obeyed to the fact that the results thus obtained could be concatenated with the mixing process to be described below, in such a way that the result of this combination could be compared with that of the chemical-potential centered analysis represented by eq. (43).

10. The mixing process

It was Lord Rayleigh the first to recognize that work might be obtained by the isothermal mixing of gases. In a paper titled "On the work that may be gained during the mixing of gases," published in 1875, he demonstrated, in the words

of Darrigol (2018), that “... the maximal work that can be obtained by mixing (isothermally) two gases initially occupying the separate volumes V_1 and V_2 and finally sharing the volume $V_1 + V_2$ is equal to the work produced by the expansion of the first gas alone from V_1 to $V_1 + V_2$ plus the work produced by the expansion of the second gas alone from V_2 to $V_1 + V_2$. The maximal work is reached when the mixing is reversible.”

The following discussion pertains the isothermal and reversible mixing of the product of the first concatenation, that is, of the $(1 - \pi)\alpha(1\text{bar}, T)$ moles of α in cylinder C_α , and the $\pi\beta(1\text{bar}, T)$ moles of β in cylinder C_β . Apart from saying that this isothermal, reversible, and work producing mixing process takes place in a device in thermal contact with the same bath, and properly coupled to the same work reservoir used in the van' Hoff operation; we will add that excellent discussions about this issue are available in the thermodynamic literature (Klotz and Rosenberg, pp. 271-273, Schmidt, pp. 135-138). In them we find the mixing work given by the following equation:

$$W_{\text{sys},\text{mix}} = -(n_\alpha RT \ln x_\alpha + n_\beta RT \ln x_\beta) \quad (97)$$

In terms of the notation which based on the degree of advancement ξ , was introduced in eq. (17) of Section 2, making $n_\beta = x_\beta = p_\beta = \xi$, and $n_\alpha = x_\alpha = p_\alpha = 1 - \xi$, the previous equation becomes:

$$W_{\text{sys},\text{mix}} = -RT[(1 - \xi) \ln(1 - \xi) + \xi \ln \xi] \quad (98)$$

Applying the same change of variable to eq. (66), which gives the work produced by non-mixing standard reaction (44) in the first concatenation, we get:

$$W_{\text{sys}} = -\xi \Delta G_{\alpha \rightarrow \beta}^\circ \quad (99)$$

At the end of this mixing process, we find that the total work produced by the system amounts to:

$$W_{\text{sys},\text{tot}} = -\xi \Delta G_{\alpha \rightarrow \beta}^\circ - RT[(1 - \xi) \ln(1 - \xi) + \xi \ln \xi] \quad (100)$$

In terms of free energy, the two previous equations find, on reason of eq. (5), the following equivalent expressions:

$$\Delta G_{\text{sys}} = \xi \Delta G_{\alpha \rightarrow \beta}^\circ \quad (101)$$

$$\Delta G_{\text{sys},\text{tot}} = \xi \Delta G_{\alpha \rightarrow \beta}^\circ + RT[(1 - \xi) \ln(1 - \xi) + \xi \ln \xi] \quad (102)$$

A simple inspection will reveal the identity existing between equations (43) and (102), confirming this way the equivalence of the usual thermodynamic procedure with that of the van't Hoff equilibrium box.

11. Discussion

11.1 The previously noted fact that reaction (44) as it takes place in the van't Hoff equilibrium box transits from an initial state represented by 1 mole of pure butane in cylinder C_α to a final state represented by $(1 - n)$ moles of pure butane in the same cylinder, and n moles of pure isobutane in cylinder C_β , both at 1 bar of pressure at the selected temperature, is what makes of this reaction a standard reaction:

The word 'standard' refers not to any particular temperature, but to unit pressure of 1 bar for each of the pure reactants and products." (Denbigh, p. 148)

The 'pure' condition means, of course, unmixed.

The standard path for reaction (44), a non-mixing path, is thus the one defined by eq. (101). The fact indicated by Table 2 that $\Delta G_{\alpha \rightarrow \beta}^0 = -3747.1 \text{ J mol}^{-1}$, allows to write this equation in the following manner

$$\Delta G_{sys} = -3747.1n = -3747.1\xi \quad (103)$$

Any point on the negatively sloped line defined by this equation on coordinates $\Delta G_{sys} - \text{vs. } -\xi$ corresponds this way to a different run of reaction (44); Each of these runs, characterized by a given n or ξ , producing a different change in the Gibbs energy of the system, and a different work output. The fact that for all n different from zero, $0 < n \leq 1$, it is true that $\Delta G_{sys} < 0$, means that reaction (44) is spontaneous for all these n .

The fact that the linear path of reaction (44) is negatively sloped or, equivalently, a Gibbs energy decreasing path, means that any number of moles of α introduced into the van't Hoff box will be totally converted into the stoichiometrically corresponding moles of β .

It is interesting to note here that this devoid of mixing, and full-conversion standard reaction comes out of the equilibrium mixture of the same reaction, a reaction which precisely on reason of having taken place along a mixing path, was incapable of complete conversion.

11.2 As proved above, the mixing of the products of reaction (44) transforms the path of reaction (44) from one described by eq. (101) to one described by eq. (102). The graph of this equation takes the familiar form of the concave up curve with its minimum corresponding to the equilibrium mixture.

Of the two sources capable of providing energy for reversible reaction (1) to transform into mechanical work, it is the one coming from the chemical process itself, that is, the one associated to the breaking and forming of bonds ($n\Delta G_{\alpha \rightarrow \beta}^o$) the one with which the standard reaction deals with. The 'actual' path of a chemical reaction, deals with both, the previous one, and the one originating in the mixing process ($n_{\alpha}RT \ln n_{\alpha} + n_{\beta}RT \ln n_{\beta}$).

11.3 In thermodynamics, reversible is any process driven by an internal force infinitesimally larger than an external resisting force of the same nature. Thus, the reversible expansion of a gas requires the pressure of the gas being infinitesimally larger than an external, resisting pressure. For example, maximum work is obtained from a chemical reaction taking place in an electrochemical cell working "against an external voltage lower than its own by no more than a differential amount" (Pimentel & Spratley, p. 112).

The fact that in chemical reactions with non-ionic mechanisms, say the gas-phase reaction above considered, it is apparently impossible to oppose a force of the same nature to the one driving the reaction, that is, to the one which called the 'chemical force' and represented by f , finds definition in terms of the difference of the stoichiometrically weighted chemical potentials of reactants minus products, seems to be the reason why the only practical path open to the reversibility of these reactions is the one represented by the van't Hoff equilibrium box in which the reaction of interest is seen taking place 'at equilibrium'. The reason why this is so simple: A reaction taking place at equilibrium does so with a chemical force equal to zero. In this case the opposing force is redundant, there is just no need for it given that there is nothing for it to oppose.

11.4 We have already proved the usefulness of equation $dW = f d\xi$ for the quantification of the work produced by a reversible reaction along any given transit $\xi_1 \rightarrow \xi_2$. The interesting thing to note in this regard is that the work coming out of the van't Hoff equilibrium box does so without the intervention of this force. It could not have been otherwise given that the reaction in it is taking place 'at equilibrium,' condition where this force becomes equal to zero. What we find instead is that the work coming out is actually PdV work. The 'interesting' qualifier used above pertains the fact that the work coming out of a reaction taking place without any change in volume, such as reaction (1), finds evaluation via $dW = PdV$.

11.5 The van' Hoff equilibrium box is a tool devised for the theoretical analysis of chemical reactions, with no possibility of practical realization. Even if you succeed in creating infinitesimal gradients, you will have to wait an infinite amount of time for the process to conclude. If these two restrictions were not enough, the case of the equilibrium box faces the additional problem of availability of the required semi-permeable membranes. These are the reasons why instead of using the equilibrium box to produce, for example, mechanical work out of the Gibbs energy change associated to the reversible oxidation of methane in a van't Hoff engine, we are forced to use its enthalpy change for this purpose, and this is done by burning it and feeding the heat thus produced to a less efficient, finite-time, thermodynamic cycle (Denbigh, pp. 72-76), a path associated to an undesirable subproduct: pollution. Let me note in this regard that the theoretical foundation provided by a corrected and extended version of quantum chemistry called Hadronic Chemistry has made possible the development of new clean energies and fuels (Santilli, 2001). This discipline, composed of three branches: Isochemistry, directed to the representation of closed isolated systems such as molecular structures; Genochemistry, directed to the description of "... irreversible chemical processes with unrestricted interactions, as expected in chemical reactions." (ibid, xl), and Hyperchemistry, directed to the representation of "... irreversible biological structures with multi-valued unrestricted internal processes." (ibid, xli), has developed new models for the hydrogen and water molecules in agreement with "... conceptual, theoretical, and experimental evidence." (Santilli & Shillady, 1999, Santilli & Shillady, 2000, p. 81)

12. The van't Hoff equilibrium box as the chemical counterpart to Carnot's heat engine

Carnot's reversible heat engine produces work out of heat flowing from a hot reservoir of temperature T_h to a cold reservoir of temperature T_c , and does it by introducing between these reservoirs what is called a Carnot engine, basically a working substance, say one mole of an ideal gas, which contained in a cylinder fitted with a frictionless and weightless piston properly connected to a mechanical reservoir, is subject to the cyclical concatenation of four reversible processes. 1) an isothermal and reversible expansion at the temperature of the hot reservoir. The conditions of the gas in this process change from (T_h, V_A) to

(T_h, V_B) ; 2) an adiabatic and reversible expansion lowering the temperature of the gas to that of the cold reservoir; the conditions of the gas transit here from (T_h, V_B) to (T_c, V_C) ; 3) an isothermal and reversible compression at the temperature of cold reservoir, changing the conditions of the gas from (T_c, V_C) to (T_c, V_D) , and finally, an adiabatic and reversible compression which starting at (T_c, V_D) ends up with the gas at the same conditions it originally had at the start of the cycle, that is (T_h, V_A) . The previous four processes, in the order mentioned, will also, for reasons of economy of expression, be designated as AB , BC , CD , and DA . Each of the engine's work producing cycles starts with the hot reservoir transferring to the gas along process AB , an amount of heat Q_h . The cyclical work output will, on its part, be designated as W .

With the previous antecedents at hand, let us recognize the following salient operational characteristics of this engine:

1) Combined, adiabatic and reversible processes BC and DA make no contribution to the work output of the cycle. The reason being that the work produced by the former is exactly the amount consumed in the occurrence of the latter. For adiabatic processes, characterized by $Q = 0$, the first law reduces to $\Delta U = w$. For ideal gases, this equation can be written as $\Delta U = C_v \Delta T$. Applied to processes BC and DA , the previous equation takes the following forms: $\Delta U_{BC} = C_v(T_c - T_h)$ and $\Delta U_{DA} = C_v(T_h - T_c)$. These equations, combined, lead to $\Delta U_{BC} + \Delta U_{DA} = 0$, and on reason of the just noted identity between internal energy change and work, also to $w_{BC} + w_{DA} = 0$. Even if not contributing to the work output of the cycle, isentropic processes BC and DA are the ones making possible the cycle.

2) The previous result leads to the realization that the work output W of the cycle is the sole matter of processes AB , and CD . In the former, an isothermal and reversible expansion of the ideal gas at the temperature T_h of the hot reservoir, the whole of the heat Q_h received by the gas from the hot reservoir is transformed into an equivalent amount of work w_h which ends up in the work reservoir. Once the temperature of the gas has been taken from T_h to T_c by process BC , the gas is subject to an isothermal and reversible compression at the temperature of the cold reservoir, T_c . The work consumed to produced this change, w_c , represents a portion of the one previously deposited in the work reservoir by process AB . In line with the mandate of the first law, as it applies to this process, the work spent on it ends up as an equivalent amount of heat Q_c in the cold reservoir.

3. The difference of the temperatures at which expansion AB and compression CD take place, explains, among other things, the partial conversion into work of the heat released by the hot reservoir.

For isothermal and reversible processes AB and CD , the following equations can be respectively written: $w_h = Q_h = RT_h \ln(V_B/V_A)$ and $w_c = Q_c = RT_c \ln(V_C/V_D)$, in which case the work output of the cycle will be given by $W = w_h - w_c$. If we now bring here the equation relating the initial and final states of isentropic processes BC and DA , namely $V_B/V_A = V_C/V_D$, and with it write $w_c = Q_c = RT_c \ln \frac{V_B}{V_A}$, and once this is done, we take the quotient w_h/w_c , we will get $w_h/w_c = T_h/T_c$. This last expression, on substitution of $w_c = w_h - W$, becomes $(w_h - W)/w_h = T_c/T_h$, which on further algebraic rearrangement produces:

$$\frac{W}{w_h} = \frac{W}{Q_h} = \eta_{Carnot} = \frac{T_h - T_c}{T_h}$$

The said difference in temperatures, even if restricting the full conversion of heat input into work output, is the sine qua non condition that opens the door to the continuous transformation of heat into work in a heat engine. When the heat engine returns to its initial condition to start a new cycle, the work reservoir is found holding an additional amount of work $W = \eta_{Carnot} Q_h$ to the one it holds at the conclusion of the previous cycle. Let us now note that an isothermal and reversible ideal gas expansion has the capability to transform its heat input into an equivalent amount of work. This, however is a one-time event. Any attempt to construct a work producing cycle by concatenating this expansion with its inverse will fail on reason of the fact that at the start of the new cycle no work will be found in the mechanical reservoir, the reason being that in the isothermal and reversible compression needed to produce said cycle, the whole of the work initially outputted will be consumed making it a zero efficient cycle. No work can come out of an isothermal Carnot's cycle.

13. The van't Hoff chemical-potential engine in comparison to that of Carnot

The following arguments will refer to the operation of the van't Hoff equilibrium box, when instead of the introduction of $n\alpha(p_{\alpha,eq}, T)$ moles of butane to the vast amount of equilibrium mixture in the reaction box, and the simultaneous removal from it of $n\beta(p_{\beta,eq}, T)$, where $0 < n \leq 1$, we introduce to the said equilibrium mixture 1 mol of butane, and remove from it 1 mol of isobutane,

both at the previously indicated conditions. The benefit of this procedure is the simplicity of description afforded with it.

The form adopted by the four processes constituting the operation of the van't Hoff engine in this new case are the following.

Process i: The isothermal and reversible expansion of the 1 mole of butane in cylinder C_α from 1 bar to $p_{\alpha,eq}$. From equations (46), and (47), this last one via the substitution $n = 1$, we get:

$$\Delta U_{sys,i} = 0 \quad (104)$$

$$-Q_{bath,i} = Q_{sys,i} = W_{sys,i} = -W_{sys,i} = -RT \ln(p_{\alpha,eq}) \quad (105)$$

Process ii: The introduction of 1 mole of $\alpha(p_{\alpha,eq}, T)$ to the vast amount of equilibrium mixture in the reaction box, and the simultaneous removal from it of 1 mole of $\beta(p_{\beta,eq}, T)$. For the reasons already given in regard to processes 2, and II, we will have that:

$$W_{\alpha,2i} = 0 \quad (106)$$

$$W_{\beta,2i} = 0 \quad (107)$$

$$W_{sys,2i} = W_{\alpha,2i} + W_{\beta,2i} = 0 \quad (108)$$

$$\Delta U_{sys,2i} = \Delta U_{\alpha,2i} + \Delta U_{\beta,2i} = 0 \quad (109)$$

$$Q_{bath,2i} = Q_{sys,2i} = 0 \quad (110)$$

Note that at the end of this process while cylinder C_α is empty, C_β contains 1 mole of $\beta(p_{\beta,eq}, T)$

Process 3i: Equilibrium is restored in the vast amount of reaction inside the reaction box via the occurrence at equilibrium of the following reaction.



The 'at equilibrium' nature of the previous reaction means, as already discussed, that:

$$W_{sys,3i} = 0 \quad (111)$$

From equations (57) and (58), via the same substitution, we get:

$$\Delta U_{sys,3i} = \Delta U^\circ = \Delta H^\circ \quad (112)$$

$$\Delta H^\circ = Q_{sys,3i} = -Q_{bath,3i} \quad (113)$$

Process 4i. The mole of β in cylinder C_β is compressed isothermally and reversible from $p_{\beta,eq}$ to 1 bar. With base on (60) and (62) and the previously noted substitution, we get:

$$W_{sys,4i} = Q_{sys,4i} = -Q_{bath,4i} = RT \ln p_{\beta,eq} \quad (114)$$

$$\Delta U_{sys,4i} = 0 \quad (115)$$

14. Van't Hoff's chemical-potential engine compared to Carnot's heat engine

With the two previous sections in place, the following statements will be advanced:

1. The obvious difference between Carnot's and van't Hoff's engines is that while the former exploits the work producing potential subsumed by the transfer of heat from a higher to a lower temperature, the latter produces work out of the "transfer of chemical matter between two different chemical states described by chemical potentials." (Gill, p. 507). The fact that the purpose of one and the other is the same, namely the production of work, is the reason why the van't Hoff equilibrium box is being here referred to as an 'engine'.

Just like no work is outputted in the absence of a temperature gradient in Carnot's engine, neither is, in reference to a chemical reaction, when the value coming out of the combination of the chemical potentials of the reactants, properly weighted by their respective stoichiometric coefficients turns out to be identical to that of a similar combination of the chemical potentials of the products. In both cases the reason is the same: from a system in equilibrium (thermal in the former, and chemical in the latter) no work production is possible.

2. A closer look at equations (105), (108), (111), and (114) allows us to realize that the work output of van't Hoff's engine finds quantification in precisely the same way it happens in Carnot's engine, that is, in terms of the combination of the work produced by an isothermal and reversible expansion, and the work consumed by an isothermal and reversible compression. The difference being that while in Carnot's engine they take place at different temperatures, in van't Hoff's engine they take place at the same temperature.

3. In a heat engine it is the no-work-contributors adiabatic and reversible processes the ones making the reversible cycle possible. They break the finite temperature gradient into an infinity of steps differing infinitesimally in temperature, and in doing so providing, via the working substance, a reversible

connection between them. Once a cycle concludes via process DA , the engine is ready to start a new one in which, again, one portion of its heat input Q_h will be transformed into mechanical work, with the rest discarded into the cold reservoir as the amount of heat $Q_c = Q_h - W$, and so on for each other cycle.

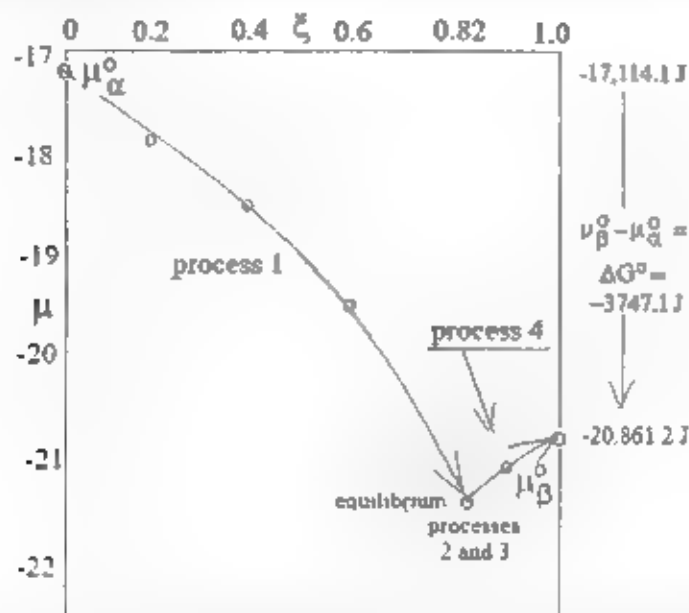


Figure 4. The reversible transit of $1\alpha(1 \text{ bar}, T) \rightarrow 1\beta(1 \text{ bar}, T)$ in a van't Hoff engine is here shown taking place via the concatenation of work-producing isothermal and reversible expansion 1, work-less processes 2 and 3 jointly representing the 'at equilibrium reaction', and work-consuming isothermal and reversible compression 4.

In van't Hoff's engine, on the other hand, it is the 'at equilibrium reaction' —which for the sake of this argument will be taken as the combination of processes 2i and 3i (after all, reaction 3i won't take place without the previous occurrence of process 2i) the one which, 1) in combination with work-producing process 1i, and work consuming process 4i, provide the reversible path to the transit of chemical matter from μ_α^0 to μ_β^0 ; and 2) by itself makes possible the cyclical operation of van't Hoff's engine. The reason behind this last assertion comes from the fact that the infinitesimal displacement which in the equilibrium condition of the vast amount of reaction in the reaction box is produced by the

addition to it of 1 mole of α , and the simultaneous removal from it of 1 mole of β , finds itself cancelled by the opposite-direction displacement through which said reaction recuperates its initial equilibrium condition via the consumption of the mole in excess of α in order to replenish the lacking mole of β . At this point, it should be noted, with equilibrium restored, the reaction mixture is in the condition to perform a new cycle which starts, as before done, with the addition of a new mole of α and the removal of 1 mole of β . Each cycle responsible for the output of an amount of work $W = -\Delta G_{\alpha \rightarrow \beta}^0$.

Figure 4 provides a graphical representation of this operation.

From equations (105) and (114), in combination with the following data, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $T = 298.15 \text{ K}$, $p_{\alpha,eq} = 0.18 \text{ bar}$, and $p_{\beta,eq} = 0.18 \text{ bar}$, these last two items from Table 3, we get:

$$w_{sys,i} = 1 \cdot 8.314 \cdot 298.15 \cdot \ln(1/0.18) = 4250.67 \text{ J}$$

$$w_{sys,4i} = 1 \cdot 8.314 \cdot 298.15 \cdot \ln(0.82) = -491.92 \text{ J}$$

The algebraic summation of these two results produces the work output W of van't Hoff's engine:

$$W = w_{sys,i} + w_{sys,4i} = 4250.67 - 491.92 = 3758.5 \text{ J} \quad (116)$$

The number obtained above for W differs from the expected result, namely $-\Delta G^0 = 3747.1 \text{ J}$, in 11.4 J, or 0.3%, a reasonable difference explainable in terms of rounding off error.

In a first approximation we could use, save further pondering on this issue, the procedure used in Carnot's engine to determine the efficiency of the present operation of van't Hoff's engine; Thus:

$$\eta_{van't Hoff} = \frac{W}{w_{sys,i}} = \frac{3758.5}{4250.67} = 0.88 \quad (117)$$

As evinced by the figure, process $4i$, the one following the equilibrium restoration of the reaction in the reaction box, is non-spontaneous, and as such work-consuming. The removal of 491.92 J out of the 4250.67 J available in the mechanical reservoir are required to be spent to carry on this compression. The operation of the van't Hoff box will be now complete, with an amount of available work in the mechanical reservoir of 3758.5 J.

15. There is one aspect of the previous graph that needs clarification, and it is the one related to the fact that while the numbers used to draw the paths of processes $1i$, and $4i$ in Figure 4 are those which quoted in Table 3 refer to the

reversible, mixing-included-evolution of reaction (1); the ones that should be defining said paths are those coming out of the isothermal and reversible expansion (process 1i) and compression (process 4i) of pure ideal-gases α and β , respectively. To understand that the values of Table 3 are common to both these instances starts by recognizing that the act of *fixing* the value of ξ to be substituted in the equations for the chemical potentials of these substances (equations (30) and (31)) defines a particular mixture of given partial pressures of butane and isobutane. In this mixture no more change takes place. Asserting the contrary implies, contrary to assumption, that ξ can change. It is its unchanging nature what makes of it indistinguishable from a simple, non-reacting mixture of the said gases at the said concentrations or partial pressures: $p_\alpha = (1 - \xi)$ bar for butane, $p_\beta = \xi$ bar for isobutane. But in this simple mixture of ideal-gases we have, in accord with J. W. Gibbs (p. 157), as well as Dalton's law, that each ideal-gas is as a vacuum to the other, or, equivalently, each gas behaves as if it were alone (pure) in the total volume of the mixture at the temperature of the reaction. Thus, the chemical potential of butane in that *reaction mixture* characterized by $\xi = 0.3$ in which, in accord with eq. (17), 0.7 moles of butane exert a partial pressure of 0.7 bar at the temperature of the reaction, is identical to the chemical potential of 0.7 moles of pure butane in the volume of the mixture at the same temperature. The total pressure exerted by 0.7 moles of pure butane at temperature T when confined in a volume V , of magnitude $P_\alpha = 0.7 (RT/V)$, turns out to be identical to the partial pressure exerted by the same amount of gas in the reaction mixture at the same volume and the same temperature: $p_\alpha = 0.7 (RT/V)$:

$$\begin{aligned}\mu_\alpha(\text{pure}, P_\alpha = 0.7 \text{ bar}, T) &= \mu_\alpha(\text{mixed}, p_\alpha = 0.7 \text{ bar}, T) \\ &= \mu_\alpha^0 + RT \ln(0.7) \quad (118)\end{aligned}$$

In the words of Gibbs (p. 158) "... the potential μ_1 has the same value in the gas mixture and in the gas G_1 existing separately as supposed." An exemplification of this notion can be found Castellan (p. 224-224).

The argument leading to eq. (118) is the theoretical foundation of Smith and Van Ness explanation made in regard to the zero Gibbs energy change of process 2:

$$\begin{aligned}\text{If } \mu_\alpha(\text{pure}, P_{\alpha,eq}, T) &= \mu_\alpha(\text{mixed}, p_{\alpha,eq}, T), \\ \text{then } \Delta\mu_{sys,2} &= \mu_\alpha(\text{mixed}, P_{\alpha,eq}, T) - \mu_\alpha(\text{pure}, p_{\alpha,eq}, T) \\ &= 0 \quad (119)\end{aligned}$$

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